

L069,951



# PATENT SPECIFICATION

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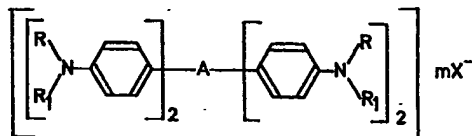
## COMPLETE SPECIFICATION

### Aminium and Diimonium Salts of N,N,N',N'-Tetrakis (p-Substituted-Phenyl)-p-Phenylenediamines and Benzidines and their use as Infrared Absorbers

We, AMERICAN CYANAMID COMPANY, a corporation organised under the Laws of the State of Maine, United States of America, of the Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new class of aminium and diimonium salts of N,N,N',N'-tetrakis (p-substituted-phenyl)-p-phenylenediamines and benzidines.

The compounds of this invention may be represented by the following formula I:

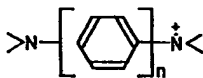


10

wherein A is

(Formula I)

10

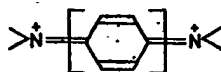


15

n is 1 or 2 and m is 1, or A is

and

15

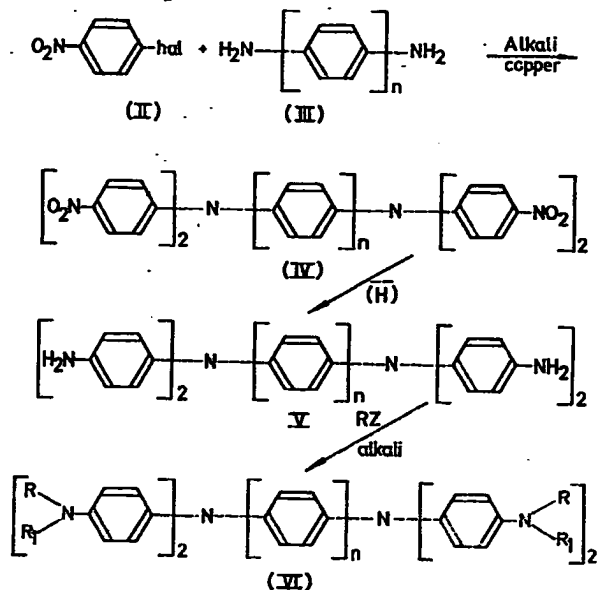


and m is 2,

R is an allyl group or a straight or branched chain alkyl group of one to twelve carbon atoms, R<sub>1</sub> is hydrogen or R, and X represents an anion.

It will be noted that the salts of formula (I) are derivatives of two similarly N,N'-substituted diamino compounds; i.e., *p*-phenylene-diamines (where n=1) and benzidines (wherein n=2).

The compounds of formula (I) may be prepared from readily available starting materials by reactions which will now be described. First of all the corresponding nitro compounds are prepared as illustrated in the following reaction scheme (A), which also illustrates reactions by which the nitro compounds are converted to the "amino" and then substituted "amino" compounds:



wherein "R", "R<sub>1</sub>" and "n" have the same meaning as above. Compounds of formulae IV, V and VI form the subject of our co-pending Application No.: 30644/66 divided herefrom.

In the foregoing formulae I and VI, the several "R's" and "R<sub>1</sub>'s" may be the same or different members of the defined groups.

Reaction of a *p*-nitrohalobenzene of formula (II) with a *p*-phenylenediamine or benzidine of formula (III) is carried out in a solvent, preferably dimethylformamide, in the presence of an alkali, such as sodium or potassium carbonate, and optionally and preferably, in the presence of copper powder, as is described in greater detail in our aforementioned co-pending Application No.: 30644/66 (Serial No. 1,069,952).

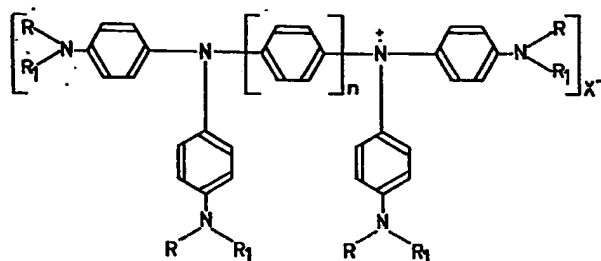
Compounds of formula (V) i.e., the "amino" compounds are readily prepared by reduction of "nitro" compounds of formula (IV), whilst the "substituted amino" compounds of formula (VI) may be prepared by reaction of the "amino" compounds with the reactant RZ which may, for example, be an alkyl halide, an allyl halide or an alkyl arylsulfonate, in the presence of a solvent and an alkali or alkaline salt. Such reactions are described in greater detail in our aforementioned co-pending Application No.: 30644/66 (Serial No. 1,069,952).

Conversion of intermediates of formula (VI) to the salts of formula (I) is by oxidation of the substituted amino compounds. This is carried out in organic solvent solution by reacting the *p*-phenylenediamine or benzidine compound of formula (VI) with a silver salt.

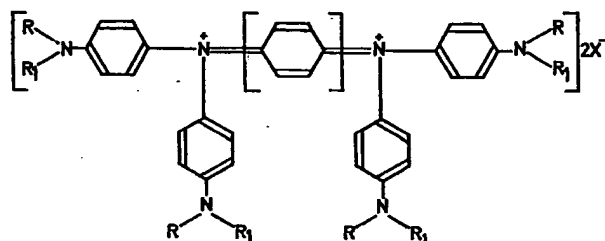
Dimethylformamide is a good solvent for use as the reaction medium. Others, such as acetone may be used. A wide variety of silver salts may be used. These include the perchlorate (ClO<sub>4</sub><sup>-</sup>), fluoroborate (BF<sub>4</sub><sup>-</sup>), trichloroacetate (CCl<sub>3</sub>COO<sup>-</sup>), trifluoroacetate (CF<sub>3</sub>COO<sup>-</sup>), picrate (NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O<sup>-</sup>, hexafluoroarsenate (AsF<sub>6</sub><sup>-</sup>), hexafluoroantimonate (SbF<sub>6</sub><sup>-</sup>), benzenesulfonate (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup>), ethanesulfonate (C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>-</sup>), sulfate (SO<sub>4</sub><sup>-</sup>) or chloride (Cl<sup>-</sup>).

It will be noted that the aminium and diiminium salts of formula (I) are derivatives of two series of similarly N,N'-substituted diamino compounds, of formula (VI); i.e., *p*-phenylene-diamines (where n=1) and benzidines (where n=2).

Oxidation of one amino group of compounds of formula (VI) produces "aminium" compounds of the following formula (VII);



5 Oxidation of two amino groups of compounds of formula (VI) wherein n is 1 gives diiminium compounds of the following formula (VIII); 5



wherein R, R<sub>1</sub>, and X are as defined above.

10 Various "aminium" compounds such as tris(p-dialkylaminophenyl)aminium salts previously have been proposed for use in various substrates to decrease transmission in the infrared region of the spectrum. Such salts do absorb strongly in the "near" 10 infrared region of the spectrum. However, most effective protection occurs in the vicinity of 960 millimicrons. Suitable compounds capable of broad absorption at longer wavelengths in the near infrared have been desired but in the past have not been available.

15 It has now been found that many of the compounds of this invention absorb broadly in the near infrared region of the spectrum at wavelengths longer than those obtained with compounds previously available. Improved absorption is obtained in the region of longer wavelengths between about 1000 and about 1800 millimicrons. Many 15 of the compounds also have desirable absorption at shorter wavelengths in the near infrared region. These compounds also transmit a useful amount of visible light.

20 Radiant energy from the sun is frequently grouped into three regions, the near-ultraviolet, the visible and the near-infrared. Together these three regions cover the range of wavelengths of from 0.290 micron to about 5.0 microns. Somewhat arbitrarily, the near-ultraviolet spectrum may be considered to cover the region of 20 0.300—0.400 micron; the visible spectrum, the region of 0.400—0.700 micron; and the near-infrared spectrum the region of 0.700—5.0 microns.

25 Heat from the sun is essentially due to the near-infrared radiant energy. Other high temperature bodies, such as tungsten filaments, fluorescent lamps, carbon arcs, etc., also radiate energy in the near infrared region. For practical purposes, this region 25 often is defined as falling between 0.7 and 5.0 microns, this being the region where common sources of infrared radiation emit substantially all of their infrared energy. 30 Over half of the total radiation energy emitted by the sun or electrical lamps lies in the near-infrared region. This is shown in the following tables.

TABLE I

Approximate Distribution of Radiant Energy  
From Several Energy Sources

	Percent of Total Radiant Energy Emitted			
	.3—.4 $\mu$	.4—.7 $\mu$	.6—1.6 $\mu$	Above .7 $\mu$
Sunlight (reaching earth)	5	42	54	53
Tungsten Lamp, 500 w	0.1	10	53	90
Fluorescent Lamp	5	35	28	60
Carbon Filament Heater	0	1	28	99
Nonluminous Heaters	0	0	1.3	100

Accordingly, it may be seen that a large proportion of the energy transmitted by our common light sources serves no useful purpose with respect to illumination, but contributes to the development of heat in the material receiving the radiation.

TABLE II

Approximate Distribution of Radiant  
Energy of Sunlight

Region ( $\mu$ )	Percent of Total	Percent of Infrared
0.3—0.4	5	—
0.4—0.7	42	—
0.7—1.0	23	43.5
1.0—1.3	12	22.5
1.3—1.6	4.5	8.5
1.6—1.9	4.5	8.5
1.9—2.7	5	9.5
2.7—up	4	7.5

This table indicates that within the near-infrared region, the greater part of the infrared energy is radiated within the region from about 0.7 to about 2.0 microns. For example, in normal sunlight some two-thirds of the radiant energy is at wavelengths of from about 0.7 to about 1.3 microns.

It also may be noted in Table II that some 43—44% of the total infrared radiation in sunlight is in the region just above about 0.7 microns. The latter is about the upper limit of the visible range which, as noted above, usually is defined as from about 0.4 to about 0.7 microns, hence the "near" infrared designation. While by the foregoing definition the near-infrared region extends only down to about 0.7 micron, for purposes of this invention the region of particular interest extends from about 0.65 micron to about 1.3 microns. In the following discussion this region will be designated as the (NIR).

In many circumstances it is desirable to filter out nonvisible radiations of the near-infrared region without materially diminishing transmission of visible radiations. There are many potential applications for materials that will transmit a major portion of the visible radiations but at the same time be at least semiopaque to heat-producing infrared radiation, particularly that in the above-noted (NIR). Among such possible applications may be mentioned sunglasses, welders' goggles and other eye protective filters, windows, television filters, projection lenses and the like. In many, if not most, of such uses the primary object is to protect the human eye from the adverse effects of radiation in the near infrared.

Experience has shown that sunglasses, as an illustrative example, should be capable of transmitting at least 10% of incident visible light shorter than about 0.65 micron. However, to provide adequate protection for the human eye, transmission should be less than forty percent at from about 0.65 to about 0.75 micron and not

over about ten percent between about 0.75 and about 0.95 micron. Preferably, some 20% or more of visible light will be transmitted. In the two other noted ranges, preferably transmission should not exceed about five percent and one percent respectively.

Other protective optical filters may vary as to requirements in the visible range. In most cases, however, transmission in the near-infrared should not exceed the indicated limitations. This applies, for example, not only to other eye protective devices as widely different as welder's goggles and window glass, but also to protecting inanimate material as in the case of projection lenses. optimum protective utility, therefore, ordinarily requires relatively good transmission of radiation below about 0.65 micron but reduced or minimized transmission above that value. Obviously complete cutoff at exactly this, or any other wavelength, is impossible. Nevertheless, for the purposes of this invention, cutoff should be as sharp as possible within a minimum spread of wavelength at about 0.65 micron.

Various organic plastic substrates are available having generally suitable transmission properties in the visible region. Illustrative examples include; cellulose derivatives such as

cellulose nitrate and cellulose acetate; regenerated cellulose and cellulose ethers for example, ethyl and methyl cellulose;

polystyrene plastics such as

polystyrene *per se* and polymers and copolymers of various ring-substituted styrenes for example *o*-, *m*- and *p*-methylstyrene and other ring-substituted styrenes as well as side-chain substituted styrenes such as alpha-, methyl- and ethylstyrene and various other polymerizable and copolymerizable vinylidenes;

various vinyl polymers and copolymers such as

polyvinyl butyral and other acetals, polyvinyl chloride, polyvinyl acetate and its hydrolysis products and polyvinyl chloride-acetate copolymers;

various acrylic resins such as

polymers and copolymers of methyl acrylate, methyl methacrylate, acrylamide, methylolacrylamide, and acrylonitrile;

polyolefins such as

polyethylene and polypropylene; polyesters and unsaturated-modified polyester resins such as those made by condensation of polycarboxylic acids with polyhydric phenols or modified using unsaturated carboxylic acid and further modified by reacting the alkyd with another monomer;

polymers of allyl diglycol carbonate; and various copolymers using as a cross-linking monomer an allyl ester of various acids. Of particular interest and preferred herein as substrates are cellulose acetate, methyl methacrylate, polystyrenes and polymers of allyl diglycol carbonates.

Any one such substrate may, and usually does, vary from the others very appreciably in its transmission of radiant energy at various wavelengths. Nevertheless, if not modified, none meet the foregoing transmission requirements. Some additive is necessary to decrease the infrared transmission without adversely effecting transmission in the visible range.

Heat resistance of the compounds of this invention can be demonstrated when the aminium salts are dispersed in plastic materials, or when they are dissolved in solvents. They are adequately resistant to exposure to temperatures up to about 200° C. This temperature is frequently encountered in the processing of plastic substrates such as those discussed above. Accordingly, compounds of this invention are suitable for purposes of use in such cases.

Products of this invention have good light and heat stability when incorporated into organic plastic substrates. Satisfactory absorption by transparent plastics of radiant energy in the 1000 to 2000 millimicron region (as given off by the sun or by other light sources) has not been possible heretofore. This portion of infra-red radiation is a sizable portion of the total infrared radiation from sunlight, incandescent and other lamps.

In use, the compounds of the present invention may be incorporated in any suitable plastic or applied on suitable transparent substrates of plastic or glass. This is done by any of several known procedures, including for example; solution casting or dipping; hot milling; burnishing or by dyeing. Organic plastic material containing the compounds can be molded into formed articles such as sheets and plates.

In any method of use, the compounds may be incorporated as a barrier layer in or near one surface of a substrate or be disseminated therethrough. Choice of either

practice depends on the type of protection used and the physical method used to combine the substrate and the compounds.

5 Either practice can be used to protect the treated material. Either can also be used to form a protective barrier between an object to be protected and the source of the infrared radiation. In the latter case, protection is usually provided by combining the compound and organic substrate in a relatively thin layer or sheet which is then used as the protective barrier. Protection of an object also can be obtained by coating the compounds, in a suitable vehicle, directly onto substrates such as glass or formed plastic objects whether to protect the substrate or in forming a protective barrier for other objects. 5 10

It is not readily possible to assign limits to the amount which it is desirable to use. In general, the limiting maximum is only an economic one. As to the minimum, it depends on whether the compound is disseminated uniformly through the substrate or is concentrated in a barrier layer of the same or a different substrate. When disseminated through a substrate, usually to protect the latter, there should be provided at least 0.005 percent by weight of the substrate of the compound of formula I. When concentrated in a barrier layer this is equivalent to 0.01 gram per square foot of surface of a plastic substrate of 1/8 inch thickness. 15

The compounds of this invention have many uses arising from the valuable combination of infrared absorbency and transparency to visible light. These uses may be considered as falling within three major areas according to the function of the infrared absorber. 20

In the first area of use, these compounds function to filter or screen out infrared radiation and prevent its transmission through a substrate on or in which these compounds are dispersed. In this area, specific applications are in sunglasses, welder's goggles or shields, astronaut's face-plates, and face-plates in fire-fighters' reflective protective suits where transparency for vision coupled with protection of eyes from infrared radiation are desired. Also, these compounds may be incorporated in transparent plastic sheets or films for windows, doors, sky-lights, etc. in buildings, green-houses, automobiles, aircraft, ships, etc. to screen out infrared radiation and minimize heat build-up in the interiors of such structures while still transmitting visible radiation. In such applications, these compounds may be dispersed in or on a rigid plastic substrate or may be dispersed in a thin plastic film useable alone or adhered to an untreated substrate, which may be glass or plastic. For example, for automobile safety glass windshields, the plastic interlayer between the two sheets of glass may have the infrared absorber incorporated therein. Also, for store, office, or residential windows, a plastic film containing these compounds may be adhered to the glass or may be hung as a "window shade" immediately inside the window and rolled up when not needed. For sunglasses, aircraft windows, and sky-lights, these compounds may be incorporated in the plastic of which such articles are made, either as a uniform dispersion throughout or as a barrier layer adjacent one surface thereof. 25 30 35 40

In the second area of use, these compounds function to absorb infrared radiation and accumulate it as heat in order to increase the temperature of those substrate materials containing these compounds. Thus, these compounds can be incorporated onto natural or synthetic fibers used in clothing to make such clothing warmer in cold climates even though such clothing may be light in color. Also, these compounds can be dissolved in water or incorporated in plastic particles, flakes, or film strips which float on water to increase the rate of evaporation of the water (or other liquid) by solar or other infrared radiation for production of distilled water or for increasing salt concentration in the remaining liquor or for recovery of salt from solution. Further, these compounds can be incorporated into materials to improve drying rates without substantially changing the color of such materials, for example, colored inks, paints, enamels, bathing suits, etc. Likewise, incorporation of these compounds into polymerizable materials can serve to increase the rate of polymerization under infrared radiation by increasing the efficiency with which such radiation is absorbed. Also, since different colors absorb radiation at different rates, varying amounts of these compounds can be added to inks, paints, or enamels of various colors to so modify their drying rates as to make them uniform regardless of color for ease, uniformity, and economy in processing articles coated therewith. 45 50 55

60 Several processes currently in commercial operation use powdered ink formulations which are placed on paper or another substrate and fused in place by infrared radiation. In some reproduction and copying systems, the powdered ink formulations, which comprise carbon black (for infrared absorption capability and optical contrast with background) and thermoplastic polymer resins, are electrostatically attracted to

the desired location either on metal and then transferred to paper or directly on specially coated paper. In such processes, only black inks have been useable to date. The present compounds can provide the necessary infrared absorption while permitting pigments of various colors to be used in such processes. Also, powdered inks are used to provide a "raised" printing on greeting cards, match boxes, calling cards, etc. by a process which involves printing a design on paper with a clear adhesive mixture and then coating with the powdered ink which adheres only to the adhesive-printed areas. This paper is then passed under an infrared source to melt and thus fix the ink. Incorporation of these compounds into these inks can reduce the heat required in the infrared source, increase the speed with which the inks can be fused, permit a wider range of colors to be used without danger of scorching the paper background before the powdered ink is set, and permit use of light colored inks on dark colored background paper without scorching the dark paper.

Some photothermography systems of photoreproduction, such as the "Thermofax" (registered Trade Mark) system of copying, use a paper coated to make it more heat sensitive during the development of the image by exposure to infrared radiation. Incorporation of these compounds into the surface coating of the paper used for this and similar processes would make the paper even more heat sensitive without losing contrast between the printing and background making feasible lower operating temperatures or faster operation of copying devices using such paper.

Micro-encapsulation is the process of coating materials in the form of small spheres or capsules (diameters of about 1 to 200 microns) with natural or synthetic polymeric materials, such as polymethylmethacrylate. The coating retains the contents in finely divided state, in each separate sphere, until such are released for use by rupturing the capsule walls, which can be by mechanical means, such as pressure, or by application of heat, such as by exposure to radiant energy. The incorporation of the compounds of this invention into the coating makes the wall more sensitive to rupture by exposure to infrared radiation, thereby requiring less exposure time or lower intensity infrared radiation to effect rupture. Also, by use of different amounts of these compounds in the coatings of different capsules, such capsules can be made to rupture on absorption of different amounts of radiation, thereby producing a record of the relative quantities of infrared radiation impinging on any areas containing mixtures of such capsules.

Additionally, these compounds can serve to magnify the effects of infrared radiation falling on sensing elements when such elements are coated with such compounds simplifying amplification circuitry to convert signals from such elements to useable currents or voltages. Thus, sensors for fire detection devices may be so treated to make them more sensitive to the presence of flames. Also, sensors in data processing machines may be so treated to make them more sensitive to heat effects where such are used to operate electrical circuits.

In the third area of use, these compounds function by a miscellaneous assortment of mechanisms. Included in this category are such applications as incorporating these compounds into colored inks for use in ball-point or other pens so such inks will reproduce by those processes, such as "Thermofax" (registered Trade Mark), which rely on infrared absorption by the ink on the document being copied. At present, carbon black must be used, limiting the inks for such purpose to black inks. Also incorporation of such compounds into face creams and dyes for clothing and other fabrics can serve to render the wearer invisible to infrared detection devices, such as the "Sniperscope" or "Snooperscope" which operate by reflection of infrared radiation from the object, e.g., soldiers, tents, netting overguns, etc., to be detected back to a detector. Further, incorporation of such compounds into the paints used to cover non-luminous radiating surfaces, such as steam or hot water radiators, radiant heating wall, floor, or ceiling panels, etc. can serve to increase the efficiency of radiation of heat energy from such bodies to the enclosure surrounding them even though the paints are light in color or contain metal pigments.

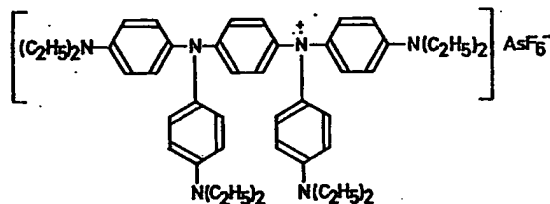
Since growth rate of plants is sensitive to the wave lengths of incident light, interposition of a film or sheet containing these compounds between such plants and the radiant energy source can serve to modify this rate. For example, germination of lettuce seeds, and the like, is promoted most at about 650 millimicrons and is inhibited most at about 730 millimicrons. By suitable selection of these compounds and concentration in such film or sheet, substantially all the radiation at 730 millimicrons can be absorbed while a high proportion of that at 650 millimicrons can be transmitted to these plants to maximize the rate of germination.

The invention will be further illustrated in conjunction with the following Examples. Therein, unless otherwise noted, all parts and percentages are by weight

and all temperatures are in degrees centigrade. For the preparation of the starting compounds used in the Examples, the reader should refer to the Examples in our aforementioned co-pending Application No.: 306,44/66 (Serial No. 1,069,952).

## EXAMPLE 1.

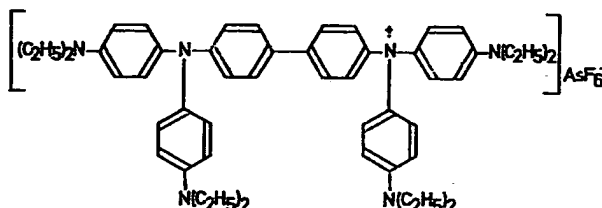
Bis(*p*-diethylaminophenyl)[N,N-bis(*p*-diethylaminophenyl)-*p*-aminophenyl]-aminium hexafluoroarsenate



To a solution of 3.49 parts (0.005 mol) of N,N,N',N'-tetrakis(*p*-diethylamino-phenyl)-*p*-phenylenediamine in 25 parts of hot dimethylformamide is added 1.49 parts (0.005 mol) of silver hexafluoroarsenate in 25 parts of dimethylformamide. After stirring for 1/2 hour, the mixture is filtered and the filtrate diluted with 350 parts of ether. On cooling in dry-ice-acetone mixture the product separates. There is obtained about 3.5 parts of green solid melting at 184°—185° C.

## EXAMPLE 2.

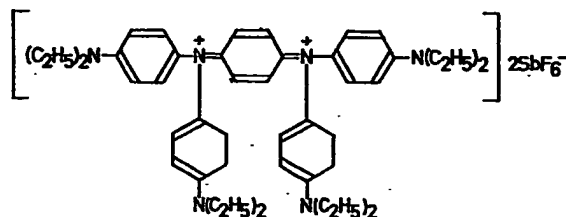
Bis(*p*-diethylaminophenyl)[N,N-bis(*p*-diethylaminophenyl)-4'-aminobiphenyl]-aminium hexafluoroarsenate



To a solution of 0.77 parts (0.001 mol) of N,N,N',N'-tetrakis(*p*-diethylamino-phenyl)benzidine in 40 parts of acetone is added dropwise with stirring a solution of 0.30 parts (0.001 mol) of silver hexafluoroarsenate in 5 parts of acetone. After stirring for about five minutes the mixture is filtered and the filtrate diluted with 200 parts of ethyl ether. On cooling in dry-ice-acetone, a green solid separates, 0.71 parts of product.

## EXAMPLE 3.

N,N,N',N'-Tetrakis(*p*-diethylaminophenyl)-*p*-benzoquinone-bis(imonium hexafluoroantimonate)



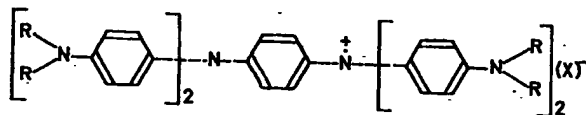
To a stirred mixture of 1.39 parts (0.002 mol) of N,N,N',N'-tetrakis(*p*-diethylamino-phenyl)-*p*-phenylenediamine is added 20 parts of acetone and 1.38 parts (0.004 mol) of silver hexafluoroantimonate. After stirring for one-half hour, the dark blue solution is filtered and the filtrate diluted with 100 parts of ether. The mixture is cooled and the solid which separates is collected, washed with ether and petroleum ether and dried. There is obtained 2.1 parts of product melting with decomposition by 216° C.



EXAMPLE 4.  
N,N,N',N'-Tetrakis(*p*-diethylaminophenyl)-*p*-benzoquinone-bis(imonium hexafluoroarsenate)

The procedure of Example 3 is followed substituting an equivalent amount of silver hexafluoroarsenate for the silver hexafluoroantimonate. The product melts with decomposition at 170° C.

EXAMPLE 5.



A series of aminium compounds of the above formula are prepared by the general procedure of Example 1 using the appropriate N,N,N',N'-tetrakis(*p*-dialkylaminophenyl)-*p*-phenylenediamine and silver salt.

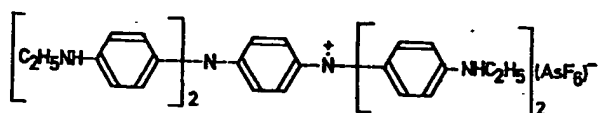
	R	X	Melting Point (°C.)
a.	CH <sub>3</sub>	AsF <sub>6</sub>	180 — 182
b.	CH <sub>3</sub>	SbF <sub>6</sub>	184 — 185
c.	C <sub>2</sub> H <sub>5</sub>	SbF <sub>6</sub>	186 — 187
d.	C <sub>2</sub> H <sub>5</sub>	BF <sub>4</sub>	170 — 172
e.	n-C <sub>3</sub> H <sub>7</sub> <sup>1</sup>	AsF <sub>6</sub>	214 — 216
f.	n-C <sub>3</sub> H <sub>7</sub> <sup>1</sup>	SbF <sub>6</sub>	215 — 216
g.	n-C <sub>4</sub> H <sub>9</sub>	AsF <sub>6</sub>	170 <sup>2</sup>
h.	n-C <sub>4</sub> H <sub>9</sub>	SbF <sub>6</sub>	175 <sup>2</sup>
i.	C <sub>8</sub> H <sub>17</sub>	SbF <sub>6</sub>	— <sup>3</sup>
j.	C <sub>12</sub> H <sub>25</sub>	SbF <sub>6</sub>	— <sup>3</sup>

<sup>1</sup> = The filtrate is diluted with an equal volume of ethanol

<sup>2</sup> = Approximate

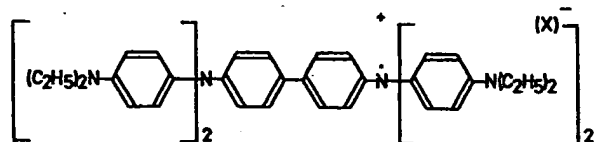
<sup>3</sup> = Not determined

EXAMPLE 6.  
Bis(*p*-ethylaminophenyl)[N,N-bis(*p*-ethylaminophenyl)-*p*-aminophenyl]aminium hexafluoroarsenate



The procedure of Example 1 is repeated substituting an equivalent amount of N,N,N',N'-tetrakis(*p*-ethylaminophenyl)-*p*-phenylenediamine for the N,N,N',N'-tetrakis(*p*-diethylaminophenyl)-*p*-phenylenediamine.

EXAMPLE 7.



Two aminium compounds of the above formula are prepared by the procedure of Example 2 substituting an equivalent amount of the appropriate silver salt for the silver hexafluoroarsenate as shown below.

Compound	X
a.	$\text{ClO}_4$
b.	$\text{SbF}_6$

5 Spectral absorption curves of organic solvent solutions of salts of this invention were determined in the visual and near infrared regions at from 0.35 to 2.00 microns. For this purpose a recording spectrophotometer fitted with a near-infrared attachment and a tungsten light source, is used. The wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) is determined from the curve. Absorptivity at the wavelength of the maximum absorption, designated ( $a_{\text{max}}$ ), is an expression of the degree of absorption. It is calculated 10 using the following relationship.

$$a_{\text{max}} = \frac{1}{bc} \log \frac{T_0}{T}$$

wherein

15 a = absorptivity  
b = the thickness of the cell (spectrophotometer) in cm.  
c = the concentration in grams per liter  
T = transmittance of light passing through the solution  
T<sub>0</sub> = transmittance of light passing through the solvent in the same cell  
20 Molar absorptivity at the wavelength of maximum absorption ( $\epsilon_{\text{max}}$ ) is an expression of the degree of absorption. It is calculated using the following relationship: 20

$$\epsilon_{\text{max}} = \frac{M}{bc} \log \frac{T_0}{T} = Ma$$

wherein

25  $\epsilon$  = molar absorptivity  
M = molecular weight of the solute  
Therefore,  $\epsilon_{\text{max}}$  is the strength of absorption based on a molar concentration of 1-gram-mol of compound per liter of solution, or it may be considered a measure of absorption of each gram-mol of compound. The larger the value of  $\epsilon_{\text{max}}$ , the greater is the absorption. 25

#### EXAMPLE 8.

30 In accordance with the foregoing discussion, spectral absorption curves of the solutions of aminium salts of Examples 1, 2, 5 & 7 in acetone are determined in the visual and near infrared regions at from 0.35 to 2.00 microns. Illustrative results are shown below. It will be noted that there are two absorption peaks in the near infrared region for the phenylenediamine derivatives of Examples 1 and 5. 30

Product of Example	Absorption Max.		
	$\lambda(m\mu)$	a	$\epsilon$
1	1450	20.9	18,500
	930	23.5	20,800
	414	22.2	19,700
5a	1325	19.2	14,900
	930	18.9	14,600
	410	19.5	15,100
5b	1310	15.6	12,800
	970	16.0	13,100
	410	16.4	13,500
5c	1450	18.7	17,400
	930	21.3	19,900
	414	19.3	18,000
5d	1440	20.7	16,200
	950	24.1	18,900
	415	21.7	17,000
5e	1460	18.4	18,400
	950	20.5	20,500
	415	18.6	18,600
5f	1460	17.1	17,900
	950	19.4	20,300
	415	17.7	18,500
5g	1460	14.1	15,700
	980	26.0	28,900
	410	16.4	18,200
5h	1420	13.8	16,000
	980	23.1	26,700
	415	16.4	19,000
2	1050	31.9	30,700
	610 <sup>(1)</sup>	3.3	3,200
	400	24.8	23,800
7a	1050	21.0	18,300
	610	2.6	2,300
	365	35.0	30,500
7b	1055	24.1	24,300
	600	2.6	2,600
	365	31.6	31,900

<sup>(1)</sup> = not  $\lambda$  max.

## EXAMPLE 9.

Spectral absorption curves of solutions of the product of Example 1 in three solvents are obtained.

<i>Solvent</i>				
<i>Acetone</i>	$\lambda$ max.	1470 m $\mu$	940 m $\mu$	414 m $\mu$
	a max.	21.5	23.9	22.7
<i>Methanol</i>	$\lambda$ max	1450 m $\mu$	950 m $\mu$	414 m $\mu$
	a max	20.9	23.5	22.2
<i>Methyl Salicylate</i>	$\lambda$ max	1550 m $\mu$	910 m $\mu$	420 m $\mu$
	a max	26.8	22.2	21.5

## EXAMPLE 10.

The product of Example 1 is incorporated into a cellulose acetate film by casting an acetone solution of the plastic and the additive on plate glass. These thin films exhibit strong near-infrared absorption having peaks at 1450 and 950 millimicrons. The light stability of the additive during exposure in an Atlas "Fade-Ometer" (registered Trade Mark) is measured spectrally. Curves are taken before and after each period of exposure. The percent additive remaining is calculated from the formula

$$\% \text{ Remaining} = A_{T/A_0} \times 100$$

wherein " $A_0$ " is the absorbance at 950 millimicrons before exposure and " $A_T$ " is the absorbance at 950 millimicrons after "T" hours of exposure.

	"Fade-Ometer"* Exposure (hours)	Additive % Remaining	
	5	99	
	15	93	
	20	86	
	30	79	
	40	73	
	50	69	

## EXAMPLE 11.

The product of Example 1 is incorporated into poly(methyl methacrylate) films in the manner described in Example 10 for cellulose acetate. The films show intense near-infrared absorption with peaks at 1450 and 950 millimicrons. The light stability of the additive is measured. \*"Fade-Ometer" is a registered Trade Mark.

	Hours of "Fade-Ometer"* Exposure	% Additive Remaining	
	5	95	
	15	33	
	20	20	

## EXAMPLE 12.

The product of Example 1 at a concentration of 0.10% (on weight of plastic) is incorporated into poly(methylmethacrylate) molding powder by fluxing on steam-heated roll mills. Chips, 74 mills in thickness, are compression molded. A transmission curve of the chip shows that the additive functions as a very effective near-infrared barrier while transmitting a considerable amount of visible light. \*"Fade-Ometer" is a registered Trade Mark.

	Wavelength (Millimicrons)		% Transmittance	
	2000	1700	1000	825
5	800	700	530	445
10	400			

## EXAMPLE 13.

The stability of the product of Example 1 during prolonged exposure to high temperatures is measured using methyl salicylate as a high boiling solvent. Dilute solutions of the additive are heated in an oil bath at various temperatures. The percent additive remaining is measured spectrally.

Temperature = 200°C.

Temperature = 210°C.

Heating time (mins.)	Additive % Remaining	Heating Time (mins.)	Additive % Remaining
5	96	5	81
8	94	8	59

## EXAMPLE 14.

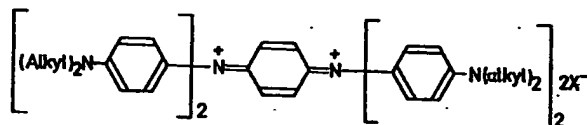
The heat stability of the product of Example 1 in a poly(methyl methacrylate) is measured as follows: films containing 0.32% of additive (on weight of plastic) are cast on plate glass from an acetone solution of the polymer and additive. The films are dried for several hours at 70° C. to remove the solvent. A transmission curve of the cast film is obtained. It is assumed that no decomposition occurs during this mild heat treatment. Sections of the cast film are compression molded between electrically heated plates at various temperatures. Transmission curves of the compression molded chips are compared to the cast film to determine the percentage of additive lost on heating.

Molding Temperature

Additive lost/minute (Average %)

160° C.	little or none
170° C.	5
180° C.	10
190° C.	15
200° C.	20
210° C.	25
220° C.	28
230° C.	35

## EXAMPLE 15.



A series of *p*-benzoquinonediimmonium salts of the above formula are prepared by the general procedure of Example 3 using the appropriate *N,N,N',N'*-tetrakis (*p*-dialkylaminophenyl)-*p*-phenylenediamine and silver salt. The substituents are summarized in the following listing:

Compound	"Alkyl"	"X"
a.	CH <sub>3</sub>	AsF <sub>6</sub>
b.	CH <sub>3</sub>	SbF <sub>6</sub>
c.	n-C <sub>3</sub> H <sub>7</sub>	BF <sub>4</sub>
d.	n-C <sub>3</sub> H <sub>7</sub>	SbF <sub>6</sub>
e.	n-C <sub>4</sub> H <sub>9</sub>	AsF <sub>6</sub>
f.	C <sub>8</sub> H <sub>17</sub>	SbF <sub>6</sub>
g.	C <sub>12</sub> H <sub>25</sub>	AsF <sub>6</sub>
h.	n-C <sub>4</sub> H <sub>9</sub>	SbF <sub>6</sub>

## EXAMPLE 16.

In accordance with the foregoing discussion, spectral absorption curves of solutions of the products of Examples 3 and 4 in acetone are determined in the near infrared region of the spectrum.

Illustrative results are shown below.

Product of Example No.	Absorption Max.		
	(mμ)	α	ε
3	1050	49.8	58,200
4	1050	55.0	59,100

## EXAMPLE 17.

The product of Example 4 is incorporated into a cellulose acetate film by casting an acetone solution of the plastic and the additive on plate glass. The thin film exhibits strong near-infrared absorption having a peak at 1075 mμ. The light stability of the additive during exposure in an Atlas "Fade-Ometer" (registered Trade Mark) is measured spectrally. Transmission curves are taken before and after each period of exposure. The percent of additive remaining is calculated from the formula

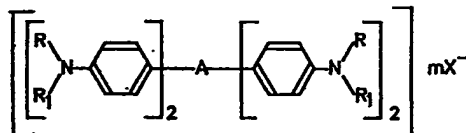
$$\% \text{ remaining} = \frac{A_T}{A_0} \times 100$$

where A<sub>0</sub> is the absorbance at 950 millimicrons before exposure and A<sub>T</sub> is the absorbance at 950 millimicrons after T hours of exposure. Illustrative results are shown below.

Exposure Time (Hours)	Additive (% Remaining)
5	80
10	72
20	65
40	54
60	47
80	41
100	33
125	26
150	21
175	15

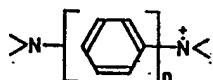
## WHAT WE CLAIM IS:—

1. A compound of the formula:



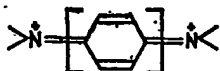
(Formula I)

wherein A is



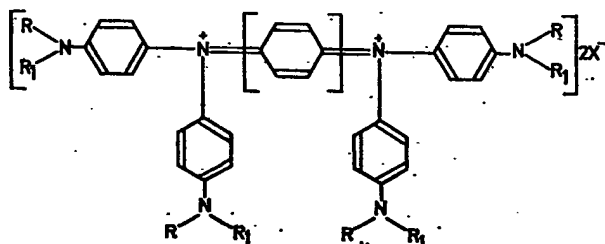
and

n is 1 or 2 and m is 1,  
or A is



R is an allyl group or a straight or branched chain alkyl group of one to twelve carbon atoms, R<sub>1</sub> is hydrogen or R, and X represents an anion.

2. A quinonediimonium salt of the formula



wherein R is an allyl group or an alkyl group of one to twelve carbon atoms, R<sub>1</sub> is hydrogen or R, and X<sup>-</sup> is an anion.

3. N,N,N',N' - tetrakis(p - diethylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroantimonate).

4. N,N,N',N' - tetrakis(p - diethylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroarsenate).

5. N,N,N',N' - tetrakis(p - dimethylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroantimonate).

6. N,N,N',N' - tetrakis(p - dimethylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroarsenate).

7. N,N,N',N' - tetrakis(p - di - n - propylaminophenyl) - p - benzoquinone-bis(imonium hexafluoroantimonate).

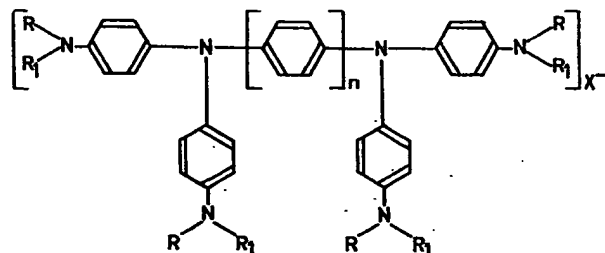
8. N,N,N',N' - tetrakis(p - di - n - propylaminophenyl) - p - benzoquinone - bis(imonium tetrafluoroborate).

9. N,N,N',N' - tetrakis(p - dibutylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroantimonate).

10. N,N,N',N' - tetrakis(p - dioctylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroantimonate).

11. N,N,N',N' - tetrakis(p - didodecylaminophenyl) - p - benzoquinone - bis(imonium hexafluoroarsenate).

12. Compounds of the formula



wherein R is an allyl group or an alkyl group of one to twelve carbon atoms, R<sub>1</sub> is hydrogen or R, n is one or two and X<sup>-</sup> is an anion.

13. Bis(*p* - diethylaminophenyl)[N,N - bis(*p* - diethylaminophenyl) - *p* - amino-phenyl] aminium hexafluoroarsenate.

14. Bis(*p* - diethylaminophenyl)[N,N - bis(*p* - diethylaminophenyl) - 4' - amino-biphenyl] aminium hexafluoroarsenate.

15. A process for preparing a compound of Formula 1 as defined in Claim 1, which process comprises reacting a *p*-phenylenediamine or benzidine compound of the formula:



wherein R, R<sub>1</sub> and n are as defined in Claim 1; with a silver salt in the presence of an organic solvent.

16. A process according to Claim 15 substantially as hereinbefore described.

17. A compound of Formula I whenever prepared by a process according to Claim 15 or Claim 16.

18. An article of manufacture comprising a substrate and a *p*-phenylenediamine or benzidine compound according to any one of Claims 1 to 14 or Claim 17 carried by the substrate.

19. An article according to Claim 18 wherein the substrate comprises an organic polymeric material and the *p*-phenylenediamine or benzidine compound is dispersed through the polymeric material.

20. An article according to Claim 18 wherein the substrate carries the *p*-phenylenediamine or benzidine compound on the surface thereof.

21. An article according to Claim 19 or Claim 20 wherein the substrate is capable *per se* of transmitting visible light.

22. A composition of matter comprising an organic polymeric material having incorporated therein at least 0.005 per cent by weight of a *p*-phenylenediamine or benzidine compound according to any one of Claims 1 to 14 or Claim 17.

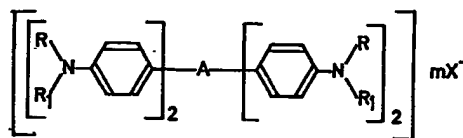
23. A composition according to Claim 22 wherein said compound is as defined in Claim 2.

24. A composition according to Claim 22 wherein said compound is as defined in Claim 12.

25. A composition according to any one of Claims 22 to 24 substantially as hereinbefore described.

26. An article of manufacture according to Claim 18 substantially as hereinbefore described.

27. A method for protecting an article against the deleterious effect of incident near infrared radiation which comprises interposing between said article and the source of said radiation a barrier layer of a compound of the formula



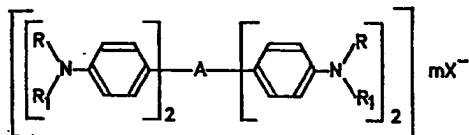
wherein A, R, R<sub>1</sub>, m and X are as defined in Claim 1.

28. A method according to Claim 27 wherein said barrier layer is carried by the article to be protected.

29. A method according to Claim 27 wherein said barrier layer is carried by a self-supporting substrate which is interposed between said article and the source of said radiation.

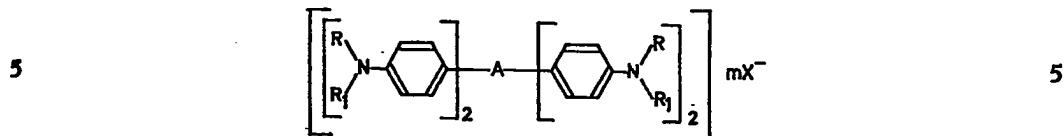
30. A method for protecting an article against the deleterious effect of incident near infrared radiation, which comprises dispersing through the article a compound of the formula





wherein A, R, R<sub>1</sub>, m and X are as defined in Claim 1.

31. A method of increasing the absorption power of a material to near infrared radiation which comprises incorporating with the material a compound of the formula



wherein R, R<sub>1</sub>, A, m and X are as defined in Claim 1.

32. A method according to any one of Claims 27—31 in which the cation is bis(*p*-diethylaminophenyl) (N,N-bis(*p*-diethylaminophenyl)-*p*-aminophenyl) aminium.

33. A method for protecting an article against the deleterious effect of incident near infrared radiation, according to Claim 27 or Claim 30, and substantially as hereinbefore described.

34. A method of increasing the absorption power of a material to near infrared radiation, according to Claim 31 and substantially as hereinbefore described.

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